

## PATENT ABSTRACTS OF JAPAN

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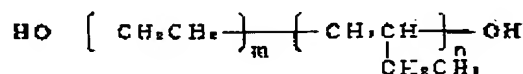
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## (54) PRODUCTION OF ISOCYANATO-CONTAINING POLYOLEFIN MODIFIER

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain an isocyanato-containing polyolefin modifier by reacting a hydroxyl-terminated poly(ethylene/butylene) copolymer with an organic diisocyanate and removing unreacted isocyanate monomer from the reaction product.

SOLUTION: A hydroxyl-terminated poly(ethylene/butylene) copolymer which is a random or block copolymer represented by the formula, has an ethylene/ butylene molar ratio m/n of 90/10 to 10/90 and has a number-average molecular weight of 500-10,000 is reacted with an organic diisocyanate under isocyanate- excess conditions. Next, unreacted isocyanate monomer is removed from the reaction product to obtain an isocyanato-containing polyolefin modifier having a free isocyanate content of below 1wt.%. This modifier is added to an adhesive or a coating material to improve its adhesion to polyolefins or added to a vinyl chloride resin, a polyolefin resin or the like to flexibilize or toughen the resin.



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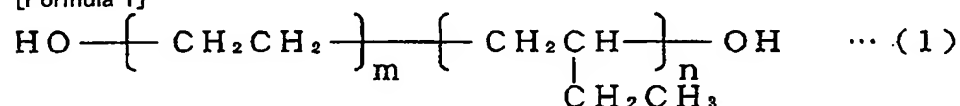
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## CLAIMS

## [Claim(s)]

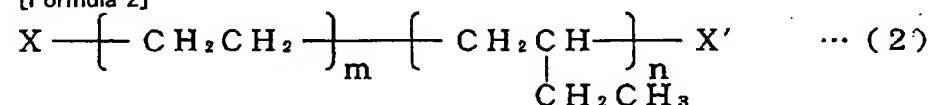
[Claim 1] It is the random copolymer or block copolymer shown by the following general formula (1). The both-ends hydroxyl-group content Pori (ethylene-butylene) copolymer and organic diisocyanate whose mole ratios (m/n of a formula (1)) of ethylene/butylene are 90 / 10 - 10/90 are made to react on the conditions that an isocyanate radical is superfluous. Then, the manufacture approach of an isocyanate radical content polyolefine system modifier acquired by removing an unreacted isocyanate monomer that the content of isolation isocyanate is less than 1 % of the weight.

## [Formula 1]



[Claim 2] In the following general formula (2), they are a random copolymer or a block copolymer. The mole ratios (m/n of a formula (2)) of ethylene/butylene are 90 / 10 - 10/90. X=OH, X'=H or X=H, and the piece end hydroxyl-group content Pori (ethylene-butylene) copolymer and organic diisocyanate that are X'=OH are made to react on the conditions that an isocyanate radical is superfluous. Then, the manufacture approach of an isocyanate radical content polyolefine system modifier acquired by removing an unreacted isocyanate monomer that the content of isolation isocyanate is less than 1 % of the weight.

## [Formula 2]



[Translation done.]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the isocyanate radical content polyolefine system modifier in which reforming of various resin is possible.

[0002]

[Description of the Prior Art] There are an epoxy resin, acrylic resin, melamine resin, polyamide resin, polyester resin, a urea-resin, phenol resin, polyurethane resin, etc. as resin used for adhesives, a coating agent, a coating, a structural material, etc. Although resin hard [ among these ] type has the advantages, such as a high degree of hardness and high endurance, there is a problem (although bond strength is large when it uses as adhesives, they are few problems of it being shocking and separating) of being inferior to flexibility or tough nature. In order to improve such a trouble, amelioration by the modifier is tried widely.

[0003] For example, as a modifier of the conventional epoxy resin, there are end carboxylation Pori (butadiene-acrylonitrile) (it abbreviates to CTBN), polypropylene glycol diglycidyl ether (it abbreviates to DGEPPG), etc. However, although toughening of resin becomes possible in CTBN reforming, the problem that weatherability will fall for the double bond contained in CTBN occurs. Moreover, in reforming by DGEPPG, there are troubles, such as causing the fall of a glass transition point or reinforcement.

[0004] Moreover, it changes to a polyvinyl chloride system ingredient from an environmental problem in adhesives, a coating agent, and the coating field, and polyolefine system ingredients, such as polypropylene and polyethylene, are being used more often in recent years. However, what has the good adhesive property to polyolefine and adhesion has endurance inadequate for conventional resin, and what has conversely good endurance has an adhesive property and inadequate adhesion.

[0005] The example which used the reactant of hydrogenation polybutadiene, the reactant of diphenylmethane diisocyanate (it abbreviates to MDI) and hydrogenation polybutadiene, and isophorone diisocyanate (it abbreviates to IPDI) for the U.S. Pat. No. 5,378,761 number official report at reforming of an epoxy resin is indicated. Moreover, hydrogenation polybutadiene, the poly isocyanate, IPDI, or the example that used the reactant with hexamethylene di-isocyanate (it abbreviates to HDI) for reforming of an epoxy resin is indicated by the U.S. Pat. No. 5,459,200 number official report.

[0006] However, on the above-mentioned specifications, it is not taking into consideration about the so-called content of the isolation isocyanate which did not participate in the reaction which exists in the obtained modifier. There are especially many isolation isocyanate contents at a resultant given in a U.S. Pat. No. 5,378,761 number official report as 3.4 - 4.1 % of the weight. Thus, if there are many isolation isocyanate contents, there is a problem in respect of an odor, and the isocyanate of this isolation will react with additives, such as a curing agent, and many physical properties will be reduced.

[0007]

[Problem(s) to be Solved by the Invention] In order to improve the conventional trouble, as a result of repeating and carrying out research examination wholeheartedly, this invention found out that the isocyanate radical content polyolefine system modifier obtained by the manufacture approach of this invention was effective, and resulted in this invention.

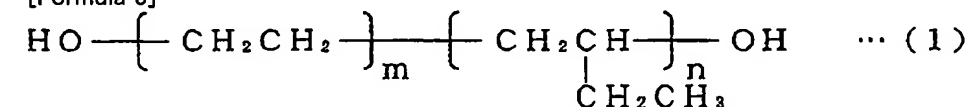
[0008]

[Means for Solving the Problem] That is, this invention is shown below.

(a) It is the random copolymer or block copolymer shown by the following general formula (1). The both-ends hydroxyl-group content Pori (ethylene-butylene) copolymer and organic diisocyanate whose mole ratios (m/n of a formula (1)) of ethylene/butylene are 90 / 10 - 10/90 are made to react on the conditions that an isocyanate radical is superfluous. Then, the manufacture approach of an isocyanate radical content polyolefine system modifier acquired by removing an unreacted isocyanate monomer that the content of isolation isocyanate is less than 1 % of the weight.

[0009]

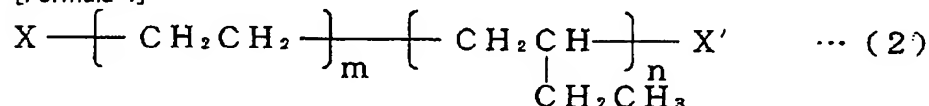
[Formula 3]



[0010] (b) In the following general formula (2), they are a random copolymer or a block copolymer. The mole ratios (m/n of a formula (2)) of ethylene/butylene are 90 / 10 - 10/90. X=OH, X'=H or X=H, and the piece end hydroxyl-group content Pori (ethylene-butylene) copolymer and organic diisocyanate that are X'=OH are made to react on the conditions that an isocyanate radical is superfluous. Then, the manufacture approach of an isocyanate radical content polyolefine system modifier acquired by removing an unreacted isocyanate monomer that the content of isolation isocyanate is less than 1 % of the weight.

[0011]

[Formula 4]



[0012]

[Embodiment of the Invention] The hydroxyl-group content Pori (ethylene-butylene) copolymer used by this invention is obtained by carrying out the graft of the vinyl system alcoholic compound to the Pori (ethylene-butylene) copolymer which is the random or block copolymer which is shown by the aforementioned formula (1) and (2), and is obtained in thing living polymerization [ like ], such as a radical polymerization, anionic polymerization, etc. of ethylene and a butylene, or processing the polymerization initiator component of an end.

[0013] The mole ratios (a formula (1) and (2) m/n) of the ethylene of a hydroxyl-group content Pori (ethylene-butylene) copolymer and a butylene are 90 / 10 - 10/90. Since the crystallinity of a copolymer becomes large and the melting point becomes high, the target modifier is hard to be obtained the case where ethylene exceeds 90-mol %, and in the case of below 10 mol %.

[0014] The number average molecular weight of a formula (1) and the hydroxyl-group content Pori (ethylene-butylene) copolymer in (2) is 500-10,000, and desirable number average molecular weight is 1,000-9,000.

[0015] When the number average molecular weight of a hydroxyl-group content Pori (ethylene-butylene) copolymer is less than 500, it is an aliphatic series system alcoholic mere compound, the reactant with organic diisocyanate has large crystallinity, and since the melting point becomes high, the target modifier is hard to be obtained. Moreover, if number average molecular weight exceeds 10,000, the reforming effectiveness will become small when a hydroxyl-group content Pori (ethylene-butylene) copolymer is used as a modifier from the first, since the viscosity of a hydroxyl-group content Pori (ethylene-butylene) copolymer becomes high the top where other resin and compatibility with isocyanate are low.

[0016] The average hydroxyl-group content of the both-ends hydroxyl-group content Pori (ethylene-butylene) copolymer in a formula (1) is 1.5-2.5 per molecule, and its 1.8-2.0 pieces are especially desirable. When a hydroxyl group is less than 1.5 pieces, it is not [ stop / \*\*\*\*\* ] a both-ends hydroxyl-group content Pori (ethylene-butylene) copolymer. When a hydroxyl group exceeds 2.5 pieces, the viscosity of the isocyanate radical content polyolefine modifier obtained becomes high, and workability worsens.

[0017] Moreover, the average hydroxyl-group content of the piece end hydroxyl-group content Pori (ethylene-butylene) copolymer in a formula (2) is 0.5-1.5 per molecule, and its 0.8-1.0 pieces are especially desirable. When a hydroxyl group is less than 0.5 pieces, it will become the blend with mere free organic diisocyanate and the mere Pori (ethylene-butylene) copolymer. For this reason, since the compatibility of a hydroxyl-group content Pori (ethylene-butylene) copolymer and organic diisocyanate is low, it dissociates and becomes scarce at stability with the passage of time. When a hydroxyl group exceeds 1.5 pieces, it is not [ stop / \*\*\*\*\* ] a piece end hydroxyl-group content Pori (ethylene-butylene) copolymer.

[0018] As said hydroxyl-group content Pori (ethylene-butylene) copolymer, there are HPVM-1202 of the concrete for example, Clayton liquid series of the product made from the U.S. shell as a random polymer type and HPVM-2202.

[0019] As organic diisocyanate used by this invention HDI, lysine diisocyanate, 2-methyl pentane -1, 5-diisocyanate, 3-methyl pentane -1, 5-diisocyanate, 2 and 2, 4-trimethyl hexa HECHIREN -1, 6-diisocyanate, Aliphatic series diisocyanate, such as 2, 4, and 4-trimethyl hexa HECHIREN -1 and 6-diisocyanate, IPDI, 2, 4-cyclohexyl diisocyanate, 4, and 4'-dicyclohexylmethane diisocyanate, Alicycle group diisocyanate, such as hydrogenation xylylene diisocyanate and hydrogenation trimethyl xylylene diisocyanate, 4 and 4'-MDI, 2, 4'-MDI, 2, and 2'-MDI, 4, and 4'-dibenzyl diisocyanate, 1, 5-naphthylene diisocyanate, PARAFENI range isocyanate, Aromatic series diisocyanate, such as 2, 4-tolylene diisocyanate (it abbreviates to 2 and 4-TDI), 2, and 6-TDI, Alt.-xylylene diisocyanate, meta-xylylene diisocyanate, difficulties, such as Para-xylylene diisocyanate and tetramethyl xylylene diisocyanate, — yellowing — diisocyanate and such mixture are mentioned and desirable organic diisocyanate is advantageous HDI in price, IPDI, and TDI and MDI.

[0020] Furthermore, when a removal process depends that of isolation isocyanate on distillation, high HDI and high TDI of vapor pressure will become desirable among the aforementioned organic diisocyanate.

[0021] As a reaction catalyst at the time of compounding the isocyanate radical content polyolefine system modifier in this invention, the so-called well-known urethane-ized catalysts, such as organometallic compounds, such as dioctyl CHINJI laurate, organic amines, such as triethylenediamine, and a salt of those, can be used.

[0022] It is a rate exceeding 1, as for the mole ratio of the isocyanate radical / hydroxyl group at the time of manufacturing an isocyanate radical content polyolefine system modifier using both-ends hydroxyl-group content

Pori (ethylene butylene) in this invention, 10-100 are specifically desirable, and 20-80 are the most desirable.

[0023] It is two or more, as for the mole ratio of the isocyanate radical / hydroxyl group at the time of manufacturing an isocyanate radical content polyolefine system modifier using piece end hydroxyl-group content

Pori (ethylene butylene) in this invention, 10-100 are specifically desirable, and 20-80 are the most desirable.

[0024] 15-100 degrees C of reaction temperature are 40-90 degrees C preferably. In the case of less than 15 degrees C, since an isocyanate radical and a hydroxyl group hardly react, it will become the blend with mere free organic diisocyanate and the mere Pori (ethylene-butylene) copolymer. For this reason, since the compatibility of a hydroxyl-group content Pori (ethylene-butylene) copolymer and organic diisocyanate is low, it dissociates and it becomes scarce at stability with the passage of time. When exceeding 100 degrees C, an allophanate radical generates by the reaction of not only a urethane group but a urethane group, and an isocyanate radical, or isocyanate radicals, such as an urethodione group and an isocyanurate radical, react, and the target modifier is hard to be obtained.

[0025] The reaction approach at the time of compounding the isocyanate radical content polyolefine system modifier in this invention can be manufactured by approaches, such as the solid reacting method and the solvent reacting method. Since an isocyanate radical content polyolefine system modifier is obtained by the manufacture approach of this invention through the process which removes isolation isocyanate, there are few losses and a solid reaction with an easy removal process is desirable.

[0026] Unreacted isocyanate is removed after a reaction and isolation isocyanate carries out to less than 1% of the weight. Make it once dissolve in the distillation and the good solvent to decompress as the removal approach, it is made to distribute in the reprecipitating method which supplies this in a poor solvent next, and a poor solvent, and there is an extraction method which supplies this to a good solvent next. The removed isocyanate monomer can be collected and reused.

[0027] Thus, the isocyanate content of the isolation contained in the obtained isocyanate radical content polyolefine system modifier is less than 0.5 % of the weight preferably less than 1% of the weight.

[0028] When isolation isocyanate contains 1% or more, there is a problem on the odor by the steam of organic isocyanate and a handling operator's health. Moreover, the isocyanate of isolation reacts with additives, such as a curing agent, and has a bad influence on many physical properties.

[0029] As an application of the obtained isocyanate radical content polyolefine system modifier, it can add in adhesives, can add in the adhesive improvement to polyolefine, and coatings, and improvement in adhesion to polyolefine and flexible-ization of a paint film can be attained. Moreover, it is used for the application which adds to vinyl chloride resin, polyolefin resin, an epoxy resin, acrylic resin, etc. for structural materials, and attains elasticity-izing and toughening of resin.

[0030] When using the isocyanate radical content polyolefine system modifier obtained by this invention, the resin by which reforming is carried out, and the modifier obtained by this invention are mixed and stirred at a suitable rate, and the resin by which warms as occasion demands and reforming is carried out to a modifier is made to react. Then, a pigment, a color, an anti-oxidant, an ultraviolet ray absorbent, a viscosity stabilizer, a solvent, etc. can be blended if needed, and a coating, adhesives, a coating agent, etc. can be used in the form which suited each application.

[0031]

[Example] Although an example is used for below and this invention is concretely explained to it, this invention is not limited to these. In an example and the example of a comparison, the "section" and "%" are the "weight section" and "% of the weight." In addition, an isocyanate content is JIS. K-6806 and viscosity are JIS. The isocyanate of K-6833 and isolation was measured with gel permeation chromatography.

[0032] The both-ends hydroxyl-group content Pori (ethylene-butylene) copolymer (trade name: HPVM-2202, product made from shell) of number average molecular weight 3,600 was warmed at 32.4 section preparation and 60 degrees C in 4 opening flask which constructed example 1 agitator, a thermometer, a cooling pipe, and nitrogen gas installation tubing. 4 and 4'-MDI was made to urethane-ization-react to this at 80 degrees C by 67.6 \*\*\*\*\* for 4 hours. The obtained reactant is set to RM-1. MDI of isolation of the isocyanate content of RM-1 was 65.3% 21.9%. Next, the normal hexane extract of RM-1 was carried out, and isocyanate radical content polyolefine compound MA-1 was obtained. The isocyanate content of MA-1 was [ MDI of viscosity of 39,000cP(s) / 25 degrees C, and isolation ] 0.3% 1.83%.

[0033] To the same reactor as example 2 example 1, HPVM-2202 were warmed at 44.8 section preparation and 60 degrees C. It 55.2-sections-taught and DBTDL was made for IPDI to react at 0.02 section preparation and 80 degrees C for 4 hours following this. The obtained reactant is set to RM-2. IPDI of isolation of the isocyanate content of RM-2 was 52.5% 19.9%. Next, the normal hexane extract of RM-4 was carried out, and isocyanate radical content polyolefine compound MA-2 were obtained. The isocyanate content of MA-2 was [ IPDI of viscosity of 34,000cP(s) / 25 degrees C, and isolation ] 0.1% 2.05%.

[0034] To the same reactor as example 3 example 1, the piece end hydroxyl-group content Pori (ethylene-butylene) copolymer (trade name: HPVM-1202, product made from shell) of number average molecular weight 4,000 was warmed at 43.4 section preparation and 60 degrees C. 2 and 4-TDI were reacted in the 56.6 sections, and dibutyltin dilaurate (it abbreviates to DBTDL) was made to urethane-ization-react to this at 0.02 section preparation and 80 degrees C for 4 hours. The obtained reactant is set to RM-3. TDI of isolation of the isocyanate content of RM-3 was 54.7% 26.9%. Next, TDI of the isolation by RM-1 by thin film distillation on the conditions of 170 degree-Cx0.5torr was removed, and isocyanate radical content polyolefine modifier MA-3 were obtained. The isocyanate

content of MA-3 was [ TDI of viscosity of 37,000cP(s) / 25 degrees C, and isolation ] 0.2% 1.08%.

[0035] To the same reactor as example 4 example 1, HPVM-1202 were warmed at 48.8 section preparation and 60 degrees C. HDI was reacted in the 51.2 sections and DBTDL was made to react to this at 0.02 section preparation and 80 degrees C for 4 hours. The obtained reactant is set to RM-4. HDI of isolation of the isocyanate content of RM-4 was 49.2% 25.1%. Next, HDI of the isolation by RM-4 by thin film distillation on the conditions of 150 degree-Cx0.5torr was removed, and isocyanate radical content polyolefine modifier MA-4 were obtained. The isocyanate content of MA-4 was [ HDI of viscosity of 35,000cP(s) / 25 degrees C, and isolation ] 0.1% 1.02%.

[0036] Example of comparison 1-4RM-1-4 were made into the examples 1-4 of a comparison. Examples 1-4 and the examples 1-4 of a comparison are collectively shown in Tables 1 and 2.

[0037]

[Table 1]

	実施例 1	実施例 2	実施例 3	実施例 4
水酸基含有ポリ (エチレン -ブチレン) 共重合体(部) HPVM-2202 HPVM-1202	32.4	44.8	43.4	48.8
有機ジイソシアネート(部) 4,4'-MDI IPDI 2,4-TDI HDI	67.6	55.2	56.6	51.2
ウレタン化触媒(部) DBTDL		0.02	0.02	0.02
NCO含有量(%) 粘度 (cP/25℃) 遊離イソシアネート(%)	1.83 39,000 0.3	2.05 34,000 0.1	1.08 37,000 0.2	1.02 35,000 0.1
臭気	小	小	小	小

[0038]

[Table 2]

	比較例 1	比較例 2	比較例 3	比較例 4
NCO含有量(%) 粘度 (cP/25℃) 遊離イソシアネート(%)	21.9 9,400 65.3	19.9 8,700 52.5	26.9 9,200 54.7	25.1 10,000 49.2
臭気	小	小	刺激臭有	刺激臭有

[0039] To the 100 sections, MA-1 [ 5-section ] was added and the application examples 1-4 and example 1-4 [adhesion test] Epicoat 1009 (product made from oil-ized shell epoxy) of an application comparison were warmed at 80 degrees C for 1 hour. After blending the 5 sections of diethylamino propylamine with this as a curing agent, applied so that it might become 50 micrometers to a polypropylene plate about thickness, and it was made to harden for seven days at a room temperature, and the application example 1 was acquired. Moreover, like the application example 1, MA-2-4 and RM-1-4 were used instead of MA-1, and the application examples 2-4 and the examples 1-4 of an application comparison were acquired. It is JIS about the application examples 1-4 and the examples 1-4 of an application comparison. The cross cut adhesion test approach of K-5400 estimated the adhesion of a paint film. The amount of survival of a paint film evaluated O for 100% - 70%, and evaluated \*\* and less than 30% for 70% - 30% as x. The result of the example of combination and an adhesion test is shown in Table 3.

[0040]

[Table 3]

	応用実施例				応用比較例			
	1	2	3	4	1	2	3	4
エピコート1009 (部)	100				100			
変性剤 (部) MA-1 MA-2 MA-3 MA-4	5	5	5	5				
変性剤 (部) RM-1 RM-2 RM-3 RM-4					5	5	5	5
硬化剤 (部) ジエチルアミノプロピルアミン	5				5			
密着性試験結果	○	○	○	○	×	△	×	×

[0041] To the 100 sections, MA-1 [ 5-section ] was added and the application examples 5-8 and example 5-8 [fracture toughness measurement trial] Epicoat 1009 (product made from oil-ized shell epoxy) of an application comparison were warmed at 80 degrees C for 1 hour. The 15 sections of 4 and 4'-diaminodiphenyl sulfones were added to this, and it mixed until it became homogeneity at 120 degrees C. Slushed this mixed liquor into the mold with a width-of-face [ of 100mm ] x height [ of 20mm ] x depth of 10mm, it was made to harden in 120 degree-Cx2-hour +180-degree-Cx 4 hours, and the application example 5 was acquired. Moreover, like the application example 5, MA-2-4 and RM-1-4 were used instead of MA-1, and the application examples 6-8 and the examples 5-8 of an application comparison were acquired. 5mm slitting was put into the center section of the application examples 5-8 and the examples 5-8 of an application comparison, the 5mm crack was attached with the still sharper knife, and it considered as the test piece for fracture toughness value (K1C) measurement. It is ASTM about K1C of this test piece. It measured in E-399. The example of combination and a fracture toughness measurement test result are shown in Table 4.

[0042]

[Table 4]

	応用実施例				応用比較例			
	5	6	7	8	5	6	7	8
エピコート1009 (部)	100				100			
変性剤 (部) MA-1 MA-2 MA-3 MA-4	5	5	5	5				
変性剤 (部) RM-1 RM-2 RM-3 RM-4					5	5	5	5
硬化剤 (部) ジアミノジフェニルスルホン	15				15			
強靱性測定試験結果 K <sub>1c</sub> (MN/m <sup>3/2</sup> )	1.05	1.10	1.10	1.15	0.45	0.60	0.55	0.48

[0043]

[Effect of the Invention] It becomes possible to make elasticity-izing of the adhesive improvement to the polyolefine of a coating or adhesives, vinyl chloride resin, polyolefin resin, an epoxy resin, acrylic resin, etc. and tough nature give by using the isocyanate radical content polyolefine system modifier obtained by this invention as explained above.

[Translation done.]